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CRITICAL PROPERTIES OF
VOLATILE HYDROCARBON
MIXTURES



by

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and

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Abstract from a dissertation submitted in partial fulfillment for the degree of Doctor of Philosophy to the Horace H. Rackham School of Graduate Study of the University of Michigan.



CRITICAL PROPERTIES OF VOLATILE HYDROCARBON MIXTURES *†

By FREDERICK KURATA (Junior Member) and DONALD L. KATZ‡ (Active Member)

ABSTRACT

The critical properties of eleven volatile, hydrocarbon mixtures have been determined experimentally. The critical temperatures for these mixtures range from 54° F. to 189° F.; and the critical pressures range from 1706 lbs. per sq. in. to 2900 lbs. per sq. in.

Based on these data and on the published critical data of the binary mixtures, new correlations were devised which will predict the critical temperatures, pressures, and densities of hydrocarbon mixtures. These correlations are especially applicable to the volatile mixtures, but their use has been extended to all types of petroleum mixtures.

The average deviation for the computed and the calculated values of the critical temperatures and pressures of the complex mixtures are $\pm 4.3^\circ$ F. and ± 40 lbs./sq.in. respectively. The average deviations for the binary mixtures are $\pm 7.0^\circ$ F. and ± 30 lbs./sq.in.

Since the advent of the use of equilibrium constants in phase equilibria computations, the knowledge of the critical properties of hydrocarbon mixtures has become of increasing importance. It is known that the values of the equilibrium constants will converge to unity for a given mixture, if plotted as a function of pressure, at the critical temperature of the mixture. At a temperature other than the critical, the pressure at which the constants appear to approach unity is related to the phase behavior of the mixture.

This paper reports the phase diagrams in the region of the critical temperature and pressure for mixtures of natural gas and natural gasoline. The limits of the two-phase region and the relative amounts of vapor and liquid within this region are of particular interest since these mixtures are similar in properties to the effluents from distillate wells. The data on these mixtures have been used as a basis for a correlation of the critical temperature, critical pressure, and critical density of complex volatile hydrocarbon mixtures.

* This paper has not been presented at an Institute meeting but is published here because of its timeliness and value to chemical engineers. Discussion will be accepted up to May 1, 1943, and will be published in Volume 39, No. 3, the June 25, 1943, Number of the Transactions.

† Abstract of Ph.D. dissertation submitted by F. Kurata to the Horace H. Rackham School of Graduate Studies of the University of Michigan.

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PREVIOUS WORK

Critical loci, border curves, and volumetric data have been reported for several binary hydrocarbon systems. The critical loci for binary paraffinic hydrocarbon systems are given in Fig. 1^{2,8,9,14,16,17,18}. Numerous investigations of the phase relation of other binary systems have been published without reporting specific critical temperatures and pressures. Previous reports from this laboratory on two natural gas-natural gasoline mixtures gave critical conditions, border curves, and percentage vapor and liquid relations within the border curve.^{6,7} Bahlke and Kay¹ and White²⁵ have measured the critical conditions for naphthas and for a gasoline which does not con-

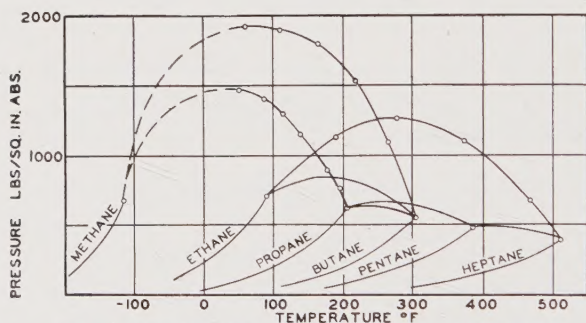


FIG. 1 CRITICAL LOCI FOR BINARY HYDROCARBON MIXTURES

tain the more volatile hydrocarbons. Roess¹⁵ has reported the most comprehensive study of the critical temperatures and pressures of petroleum fractions.

Numerous methods have been proposed for the prediction of the critical temperatures and pressures of pure compounds and of petroleum fractions.^{4,5,12,13,15,20,22,23} All of these methods of correlation were devised for pure compounds or for petroleum fractions identified by their boiling range, specific gravity, or molecular weight and were not especially applicable to mixtures containing gaseous hydrocarbons whose analysis is usually represented by percentages of pure compounds. The critical temperatures of petroleum fractions, not containing methane or ethane, are considerably above room temperature, and the critical pressure of such fractions usually are of the order of magnitude of 400 to 800 pounds per square inch. The critical pressure of mixtures containing sufficient methane and ethane to

give a critical temperature in the neighborhood of room temperature may be in the range from 1000 to 3000 pounds per square inch. This wide difference in the critical properties of the volatile hydrocarbon mixtures and petroleum fractions indicates the need for a correlation of critical properties based primarily upon volatile hydrocarbon mixtures. Mayfield¹¹ recently proposed a method for the prediction of critical temperatures and pressures of binary mixtures containing the volatile hydrocarbons. This correlation, by its nature, is limited to binary normal paraffinic mixtures, and may not be extended to complex systems such as those reported in this paper.

EXPERIMENTAL MEASUREMENTS

The experimental method for the determination of the phase diagrams and critical conditions for volatile hydrocarbon mixtures has been previously described.^{6,7} Briefly, the measurements were made in a double-glass-windowed pressure cell maintained at constant temperature in an air bath. The material charged to the cell was compressed until a single phase was reached, using mercury as a confining liquid. The pressure was reduced in steps at a constant temperature from the single phase region into the two-phase region. Visual observations of the volume of the single phase or of the vapor and liquid phases were made at each pressure. This procedure was followed for a series of isotherms at temperatures both below and above the critical temperature of the mixture. The complete apparatus was mounted on a trunnion about which the cell could be rotated to give the stirring necessary for equilibrium.

Table I gives typical experimental data observed for the mixture of natural gasoline and natural gas, $S = 4$. Figure 2 is a plot of the isotherm of liquid volume per cent as a function of pressure. Figure 3, which is a cross plot of Figure 2, is the phase diagram of the mixture; it shows the volume percentage of vapor and liquid within the two-phase region adjacent to the critical temperature and pressure.

Experimental determinations of the phase diagrams were made for seven mixtures of natural gas-natural gasoline and four mixtures of natural gas-*n*-butane. The normal butane was obtained from the Phillips Petroleum Company and was guaranteed to be of better than 99 per cent purity. Table II gives the compositions of the natural gases and gasoline used in the preparation of the mixtures investigated. The quantities of the natural gas and natural gasoline were metered into the equilibrium cell and the composition of the final

TABLE I.—TYPICAL EXPERIMENTAL DATA FOR MIXTURE

S — 4

Press. lbs. /sq.in.abs.	Volume of System, cc.	Volume of Liquid, cc.	Press. lbs. /sq.in.abs.	Volume of System, cc.	Volume of Liquid, cc.
Temperature—24° F.			Temperature—80° F.		
2336	44.3	sing. phase	2560	51.0	sing. phase
2151	44.9	" "	2475	51.7	" "
2141	45.0	44.2	2470	51.8	49.3
2125	45.2	40.8	2462	52.0	43.8
2101	45.9	38.7	2452	52.1	38.8
1988	48.7	31.5	2431	52.5	34.1
1845	53.2	28.0	2399	53.4	31.0
1662	60.8	25.3	2155	60.0	24.8
1535	67.3	23.4	1955	67.5	23.1
1288	84.5	21.5	1697	80.2	22.4
1085	106.5	19.7	1413	99.8	19.2
941	126.2	18.2	1195	121.6	17.7
848	143.8	17.6	1045	142.1	17.1
Temperature—103° F.			Temperature—109° F.		
2545	55.3	sing. phase	2683	55.3	sing. phase
2542	55.3	30.5	2562	56.7	" "
2537	55.3	30.9	2550	56.9	23.8
2535	55.5	30.0	2549	56.9	25.6
2526	55.5	29.4	2543	56.9	25.4
2501	56.0	27.8	2535	57.1	25.6
2480	56.6	27.0	2501	58.0	25.4
2462	57.1	26.4	2456	59.0	24.5
2430	57.7	25.5	2385	61.2	23.7
2288	62.1	23.7	2180	67.5	21.8
2152	66.7	22.7	1883	80.0	20.6
1780	83.2	20.0	1535	102.5	18.2
1513	100.5	18.5	1295	123.8	16.7
1287	122.0	17.2	1137	144.6	16.0
1112	143.7	16.2			
Temperature—140° F.					
2802	60.0	sing. phase			
2598	63.0	" "			
2582	63.0	" "			
2580	63.0	3.0			
2573	63.2	9.1			
2562	63.4	10.9			
2538	63.7	14.3			
2512	64.4	15.8			
2501	64.6	16.3			
2480	65.5	17.2			
2461	66.1	17.8			
2388	68.4	18.4			
2055	81.2	18.2			
1689	101.3	16.8			
1437	122.0	14.8			
1249	143.2	14.8			

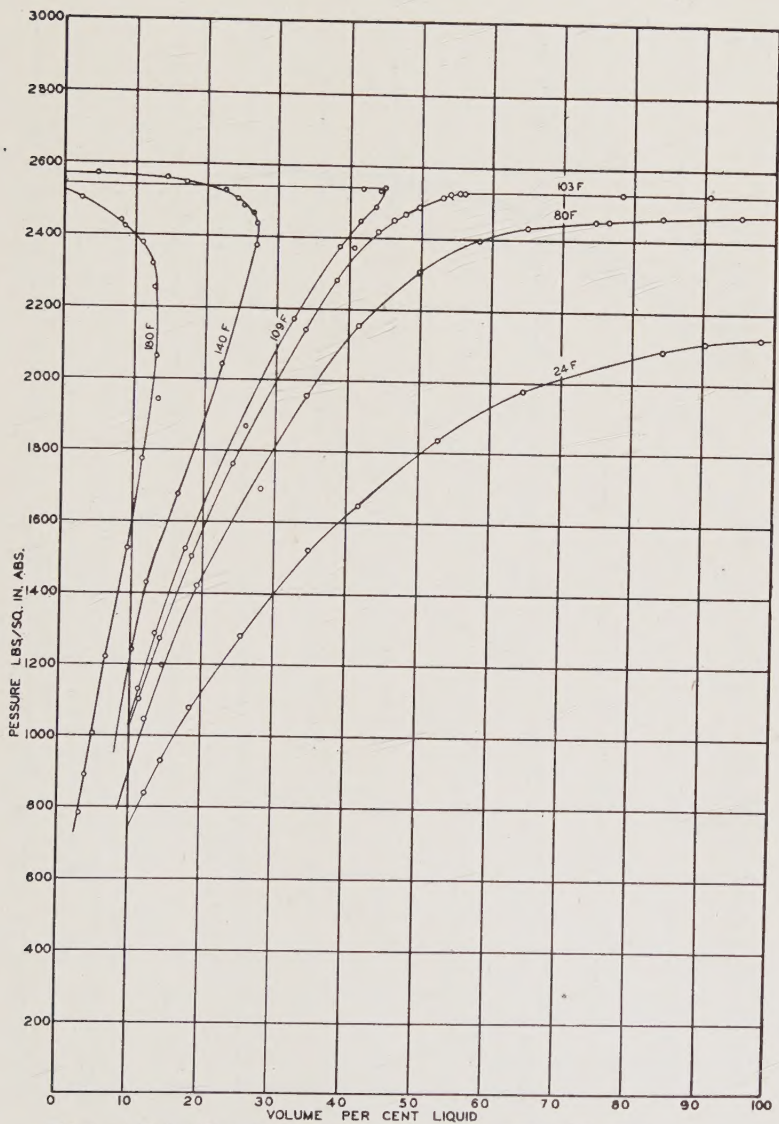


FIG 2 LIQUID VOLUME PER CENT ISOTHERMS FOR MIXTURE S-4

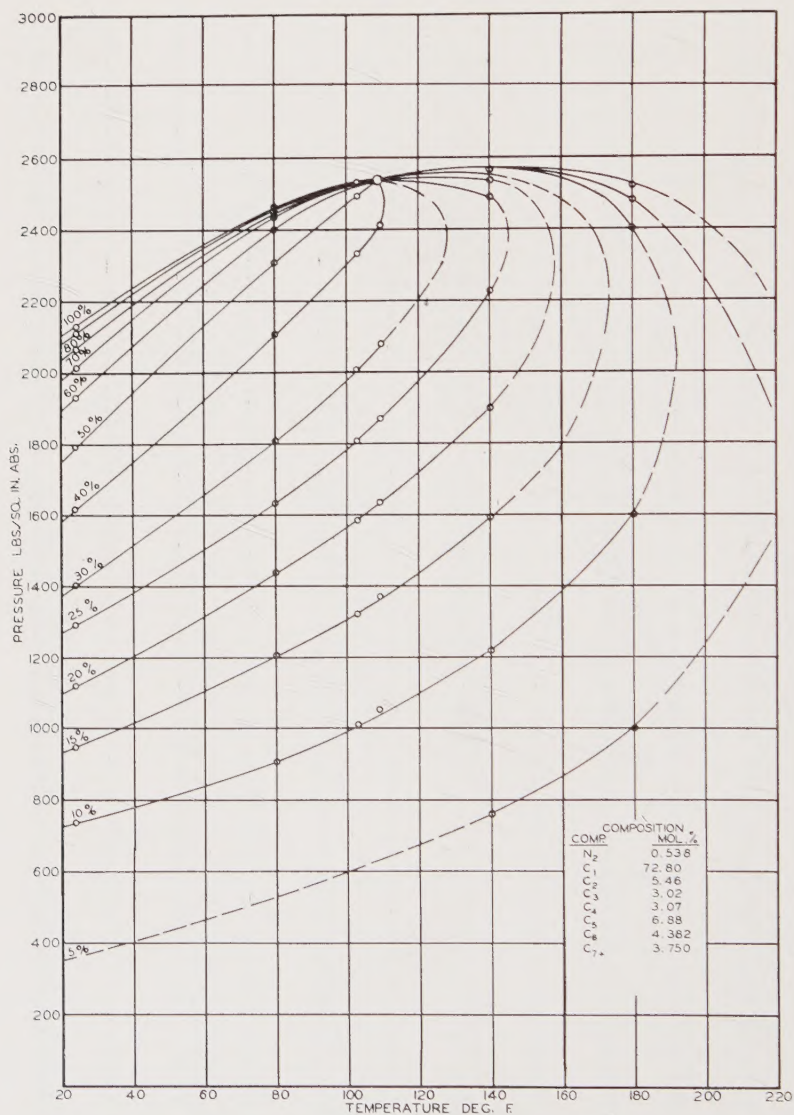


FIG 3 PHASE DIAGRAM FOR MIXTURE S-4

TABLE II.—COMPOSITIONS OF NATURAL GASES AND NATURAL GASOLINE

Compound	Natural Gas, S mol. fr.	Natural Gas, T mol. fr.	Natural Gasoline mol. fr.
Nitrogen	0.0064	0.0043	
Carbon dioxide		0.0051	
Methane	0.8641	0.9320	
Ethane	0.0647	0.0425	
Propane	0.0357	0.0161	
Butanes	0.0213		0.081
Pentanes	0.0078		0.398
Hexanes			0.281
Heptanes +			0.240
Mol. wt. heptanes +			= 106
Sp. gr. heptane +			= .733

TABLE III.—COMPOSITIONS AND PROPERTIES OF MIXTURES INVESTIGATED

Compound	Mixture S—2 mol. %	Mixture S—3 mol. %	Mixture S—4 mol. %	Mixture S—5* mol. %
Nitrogen	0.58	0.53	0.54	
Methane	78.80	62.40	72.80	59.70
Ethane	5.90	5.42	5.46	8.90
Propane	3.15	3.00	3.02	5.00
Butanes	2.66	3.10	2.07	4.90
Pentanes	4.25	7.10	6.88	9.30
Hexanes	2.52	4.56	4.38	12.20
Heptanes +	2.14	3.88	3.75	
Crit. temp., ° R.	515	569	569	629
Crit. pres. lbs./sq.in. abs.	2387	2574	2537	2615
Pseudo crit. temp. ° R.	426	463	460	515
Pseudo crit. pres. lbs./sq. in. abs.	649	635	634	621
Mol. wt.	25.0	29.5	29.1	36.2

* Previously reported (6)

mixture was computed. Table III gives the compositions of the mixtures for which the phase diagrams, critical temperatures, and critical pressures were determined. Three of these mixtures were analyzed in order to verify the metering technique; agreement within ± 0.1 mol. per cent was found for each constituent in all three mixtures. The experimental data are summarized in Table IV, which presents the temperatures and corresponding pressures along the border curve. In the two-phase region the per cent of liquid is also given.

TABLE III.—Continued

Compound	Mixture T—1 mol. %	Mixture T—3 mol. %	Mixture T—4* mol. %	Mixture T—5 mol. %
Nitrogen	0.38	0.38	0.36	0.30
Carbon dioxide	0.45	0.44	0.43	0.35
Methane	83.00	81.5	78.40	64.30
Ethane	3.76	3.72	3.55	2.94
Propane	1.44	1.41	1.36	1.11
Butanes	0.89	1.02	1.30	2.52
Pentanes	4.36	5.01	6.31	12.30
Hexanes	3.08	3.54	4.47	8.71
Heptanes +	2.63	3.03	3.82	7.47
Crit. temp., ° R.	514	525	550	649
Crit. pres. lbs./sq. in. abs....	2580	2675	2730	2900
Pseudo crit. temp. ° R.	417	425	443	522
Pseudo crit. pres. lbs./sq. in. abs.	651	647	640	607
Mol. wt.	24.5	25.4	27.6	37.7

* Previously reported (7)

Compound	Mixture B—1 mol. %	Mixture B—2 mol. %	Mixture B—3 mol. %	Mixture B—4 mol. %
Nitrogen	0.33	0.30	0.28	0.27
Carbon dioxide	0.38	0.35	0.34	0.32
Methane	70.65	65.24	61.30	58.25
Ethane	3.23	2.98	2.80	2.66
Propane	1.22	1.13	1.06	1.01
Butanes	24.20	30.00	34.22	37.50
Crit. temp. ° R.	538	576	602	610
Crit. pres. lbs./sq. in. abs....	1826	1797	1726	1706
Pseudo crit. temp. ° R.	456	482	498	512
Pseudo crit. pres. lbs./sq. in. abs.	645	639	633	629
Mol. wt.	26.9	29.3	31.2	32.5

Figure 4 presents small-scale phase diagrams of nine of the mixtures investigated and is similar to the diagram of Figure 3. The critical locus of the natural gas-butane mixtures is given in Figure 5. It may be seen that this figure is similar to the critical locus for a binary mixture such as in Figure 1, except that the border curves of these complex mixtures may extend outside the critical locus. This phenomenon is not known to occur for binary paraffin mixtures. The terminal point of the critical locus curve, representing the natural gas, was computed by the method to be presented later in the paper. Similar observations may be made on the natural gas-natural gasoline mixtures.

TABLE IV.—SUMMARY OF EXPERIMENTAL PHASE DATA

MIXTURE S — 2					
Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
20° F.		60° F.		120° F.	
100	2153	0	2417	0	2604
50	2100	30	2413	10	2564
40	1912	30	2020	10	1350
30	1574	20	1570		
20	1250	10	977		
10	758				
40° F.		80° F.		140° F.	
100	2297	0	2496	0	2613
50	2263	20	2485	10	2534
40	2095	30	2300	10	1492
30	1790	20	1747		
20	1408	10	1093		
10	865				
50° F.		100° F.		160° F.	
100	2362	0	2563	0	2603
50	2350	10	2549	10	2458
40	2215	20	2509	10	1680
30	1905	20	1956		
20	1490	10	1215		
10	920				
				180° F.	
				0	2580
				10	2150
MIXTURE S — 3					
Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
20° F.		100° F.		140° F.	
100	2049	100	2549	0	2615
80	1938	80	2547	10	2605
60	1740	60	2535	20	2580
50	1594	50	2470	20	1845
40	1423	40	2263	10	1146
30	1203	30	1953		
20	962	20	1521		
10	600	10	976		
				160° F.	
				0	2610
				10	2573
				20	2500
				20	2124
				10	1270
60° F.		120° F.		180° F.	
100	2353	0	2594		
80	2306	10	2592		
60	2200	20	2590		
50	2060	30	2582		
40	1870	40	2550		
30	1608	40	2500	0	2590
20	1276	30	2316	10	2490
10	800	20	1665	10	1492
		10	1055		

TABLE IV.—Continued

Mixture T—1					
Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
40° F.		60° F.		100° F.	
100	2402	0	2651	0	2740
60	2330	10	2651	10	2739
50	2205	20	2650	20	2738
40	2000	30	2650	30	2737
30	1745	40	2649	30	2205
20	1353	50	2565	20	1687
10	825	50	2475	10	1023
		40	2195		
		30	1838	120° F.	
		20	1453		
		10	887	0	2721
50° F.		80° F.		10	2708
100	2546	0	2728	20	2644
60	2478	10	2727	20	1843
50	2323	20	2726	10	1112
40	2096	30	2725	140° F.	
30	1790	40	2710	0	2672
20	1403	40	2440	10	2595
10	855	30	1965	20	2285
		20	1560	10	1243
		10	951	160° F.	
				0	2570
				10	2361
				10	1545
Mixture T—3					
Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
40° F.		70° F.		140° F.	
100	2505	0	2705	0	2859
50	2455	10	2704	10	2836
40	2215	20	2703	20	2760
30	1880	30	2703	20	2143
20	1445	40	2702	10	1305
10	863	40	2553		
		30	2153	160° F.	
60° F.		20	1636		
		10	976	0	2850
100	2650			10	2805
50	2625	100° F.		20	2490
40	2428			10	1460
30	2055	0	2800		
20	1572	10	2798	180° F.	
10	939	20	2795		
		30	2770	0	2785
		30	2447	10	2690
		20	1837	10	1690
		10	1100		

TABLE IV.—*Continued*

MIXTURE T — 5

Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
40° F.		120° F.		180° F.	
100	2610	100	2928	100	2920
90	2552	90	2911	90	2917
80	2473	80	2880	80	2915
70	2370	70	2820	70	2910
60	2200	60	2720	60	2900
50	2000	50	2530	50	2840
40	1725	40	2267	40	2620
30	1434	30	1900	30	2235
20	1083	20	1421	20	1700
10	673	10	850	10	1037
80° F.		160° F.		190° F.	
100	2794	100	2942	0	2901
90	2763	90	2934	10	2900
80	2705	80	2923	20	2899
70	2610	70	2909	30	2898
60	2475	60	2863	40	2897
50	2279	50	2747	40	2700
40	2010	40	2486	30	2323
30	1680	30	2103	20	1770
20	1263	20	1595	10	1080
10	755	10	970		

MIXTURE B — 1

Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
40° F.		70° F.		100° F.	
100	1763	100	1817	0	1840
70	1723	70	1809	10	1824
60	1680	60	1803	20	1780
50	1628	50	1770	20	1545
40	1511	40	1677	10	1065
30	1366	30	1530		
20	1146	20	1275		
10	740	10	876		
60° F.		80° F.		120° F.	
100	1803	0	1830	0	1823
70	1782	10	1829	10	1730
60	1765	20	1828	10	1260
50	1713	30	1827		
40	1614	30	1620		
30	1460	20	1332		
20	1225	10	930		
10	824				

TABLE IV.—Continued

MIXTURE B — 2

Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
60° F.		110° F.		140° F.	
100	1776	100	1810	0	1745
80	1700	80	1808	10	1733
60	1580	60	1801	10	1120
50	1410	50	1775	160° F.	
40	1380	40	1695		
30	1218	30	1535		
20	1012	20	1276		
10	670	10	910		
100° F.		120° F.		0	1682
100	1821	0	1790	10	1545
80	1810	10	1789	10	1360
60	1785	20	1788		
50	1731	30	1787		
40	1634	30	1613		
30	1465	20	1352		
20	1215	10	975		
10	850				

MIXTURE B — 3

Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
60° F.		120° F.		150° F.	
100	1630	100	1754	0	1714
80	1548	80	1740	10	1710
60	1403	60	1678	20	1705
50	1306	50	1608	30	1685
40	1186	40	1485	30	1565
30	1020	30	1313	20	1280
20	801	20	1065	10	904
10	429	10	713		
100° F.		140° F.		160° F.	
100	1748	100	1731	0	1695
80	1710	80	1729	10	1683
60	1607	60	1725	20	1653
50	1514	50	1705	20	1400
40	1395	40	1614	10	973
30	1220	30	1440	180° F.	
20	973	20	1188		
10	602	10	837		
				0	1645
				10	1615
				10	1130

TABLE IV.—*Continued*

MIXTURE B—4					
Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.	Vol. % Liquid	Pres.lbs./ sq.in.abs.
60° F.		120° F.		160° F.	
100	1635	100	1775	0	1670
80	1520	80	1749	10	1665
60	1390	60	1672	20	1655
50	1300	50	1600	20	1370
40	1167	40	1474	10	1030
30	996	30	1304		
20	800	20	1083		
10	513	10	785		
100° F.		140° F.		180° F.	
100	1770	100	1739	0	1560
80	1713	80	1733	10	1470
60	1602	60	1711	10	1285
50	1510	50	1676		
40	1385	40	1583		
30	1213	30	1420		
20	994	20	1188		
10	690	10	893		

This presentation of the data does not include the visual observations which accompany pressure changes in the critical region. Critical opalescence, previously described,^{6,7,26} was observed over wide ranges of temperature and pressure. By means of transmitted light a reddish-brown color was observed over a pressure range of about twenty pounds. The color first appeared just prior to reaching the border curve and disappeared after passing a short distance into the two-phase region. Small changes in pressure near the critical point could change the uniform phase into an opaque mass. Also, foaming after stirring often continued for two or three minutes before the meniscus appeared as a definition between the vapor and the liquid phase. These observations may be made anywhere within a region of $\pm 20^\circ$ F. of the critical temperature near the border curve, making it very difficult for an observer to determine the critical point for the mixture by individual visual observations. Consequently, it was necessary to plot the phase diagrams in order to accurately determine the critical points.

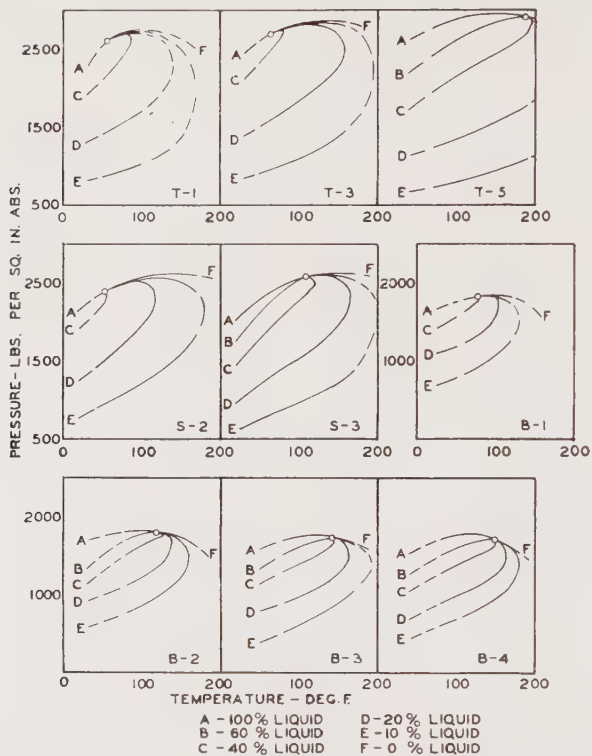


FIG 4 PHASE DIAGRAMS OF COMPLEX HYDROCARBON MIXTURES

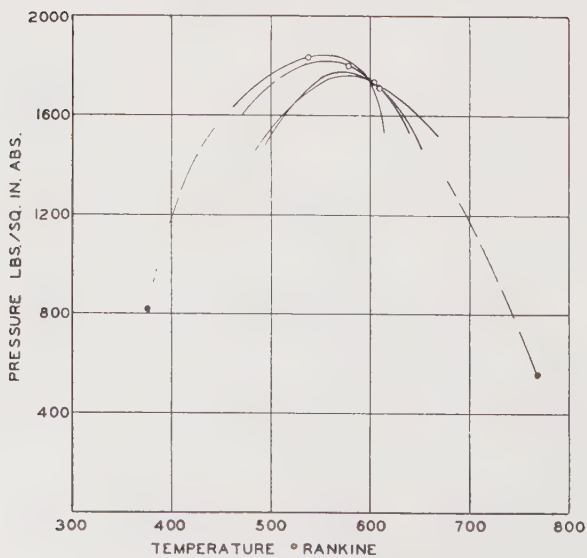


FIG 5 CRITICAL LOCUS OF NATURAL GAS N-BUTANE MIXTURES

CORRELATION OF CRITICAL PROPERTIES OF COMPLEX MIXTURES

The purpose of this investigation was to obtain data on the critical properties of complex mixtures so that a correlation could be provided for these volatile mixtures. Since the method of predicting criticals presented by Smith and Watson²⁰ was convenient and generally used for petroleum fractions, the first step appeared to be a consideration of extending this method to include the mixtures investigated. These studies resulted in a new correlation for volatile mixtures composed of pure hydrocarbons, and a combination of this new correlation with that of Smith and Watson's for mixtures containing petroleum fractions along with volatile constituents.

CRITICAL TEMPERATURE

Critical temperatures were correlated by Smith and Watson as a function of A.P.I. gravity and boiling point, using the molal average boiling point to obtain pseudo-critical temperatures and the weight average boiling point to obtain the true critical temperature. The pseudo-critical temperature used in this paper is the molal average critical temperature for mixtures of pure hydrocarbons¹⁰ and for the petroleum fractions as given by Smith and Watson.²⁰ Figure 6 is the critical temperature relationship presented by Smith and Watson. Since this chart does not predict the true critical temperature of these volatile mixtures, attempts were made to adjust the constant A.P.I. gravity lines to permit the chart to reproduce both Smith and Watson's data and those of this investigation. After this was found impossible, a new correlation for critical temperature was devised. The difficulties in adapting Figure 6 to the new data appeared in such forms as the insignificance of such terms as the liquid A.P.I. gravity and the slope of the distillation curve for normally gaseous mixtures. The variables chosen for the new correlation were molecular weight, pseudo-critical temperature, and a function to represent boiling range of the mixture.

Since the method based on these new variables is entirely empirical, an example calculation of the critical temperature of mixture, *S* — 3, has been presented in Table V to describe this correlation. The pseudo-critical temperature was computed from the analysis of the mixture and the true critical temperatures of the various constituents. Figure 7 gives the relationship between the molecular weight and critical temperature of pure paraffinic hydrocarbons and is called T_B .

equivalent critical temperature. For the mixture, *S* — 3, having a molecular weight of 29.5, Figure 7 gives an equivalent critical temperature, T_E , of 544° R. The complexity of the mixture is represented by a ratio of the equivalent critical temperature to the pseudo-critical temperature, $\frac{T_E}{pT_c}$, of 1.175. It has been found that for mix-

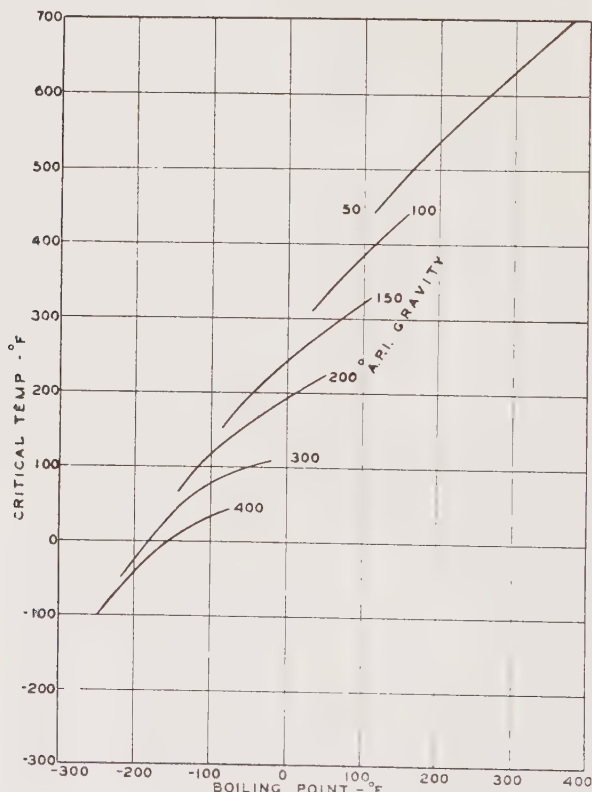


FIG 6 PSEUDO & TRUE CRITICAL TEMPERATURES FOR PETROLEUM FRACTIONS

tures containing methane such as the mixtures of this paper, a correction to this ratio must be made in accordance with Figure 8. Figure 8 gives a corrected ratio for mixture, *S* — 3 of 1.070. The critical temperature of the mixture is then obtained by means of Figure 9 when using the pseudo-critical temperature and the corrected ratio of the equivalent critical temperature to the pseudo-critical tem-

perature. For mixture *S*—3 the critical temperature is read as 572° R. or 112° F. The experimental critical temperature for this mixture was observed at 109° F.

TABLE V.—PROPERTIES OF A COMPLEX MIXTURE (*S*—3).

Constituent	Mol. Fr.	Mol. Wt.	Mol. Wt. Mix- ture	T_c °R.	pT_c	P_c lbs./ sq.in.abs.	pP_c
N ₂	0.0053	28	0.15	227	1.21	483	2.60
C ₁	0.7240	16	11.60	344	249.0	673	487.0
C ₂	0.0543	30	1.63	549	29.8	712	38.7
C ₃	0.0300	44	1.32	666	20.0	617	18.5
C ₄	0.0310	58	1.80	766	23.7	551	17.1
C ₅	0.0710	72	5.11	846	60.1	485	34.5
C ₆	0.0456	84	3.82	914	41.6	435	19.8
C ₇ +	0.0388	106	4.09	972	37.7	397	15.4
			29.5		463.2		634.6

From Figure 7 $T_E = 544^\circ \text{R.}$

Computed $T_E/pT_c = 544/463.2 = 1.175$

From Figure 8, Correct $T_E/pT_c = 1.070$

Using $T_E/pT_c = 1.070$ in Figure 9, $T_c = 572^\circ \text{R.} = 112^\circ \text{F.}$ Critical Temperature

From Figure 10 $\frac{T_c \times pP_c}{P_c} = 140$

For above mixture: $P_c = \frac{572 \times 634.6}{140} = 2585 \text{ lbs./sq.in.abs.}$

Critical Pressure.

Calculated	Experimental
$T_c = 112^\circ \text{F.}$	109°F.
$P_c = 2585 \text{ lbs./sq.in.abs.}$	$2574 \text{ lbs./sq.in.abs.}$

For mixtures of hydrocarbons not paraffinic, containing a substantial portion of petroleum fractions, or free from methane, special methods of calculating the critical temperature are required. If the mixture contains less than 5 mole per cent of methane, Figure 8 should not be used and the computed equivalent critical temperature divided by the pseudo-critical temperature should be used directly with Figure 9 to obtain the critical temperature of the mixture. This relationship appears awkward, but has been found necessary when considering the binary hydrocarbon systems and petroleum fractions along with the data of this report. If the molecular weight of the

heptane and heavier fractions is in excess of 110, the pseudo-critical temperature of this mixture should be obtained from Figure 6 in accordance with the method presented by Smith and Watson. This pseudo-critical temperature must be multiplied by the mole fraction of the heptane and heavier fractions just as the mole fractions of known constituents are multiplied by their critical temperatures. The

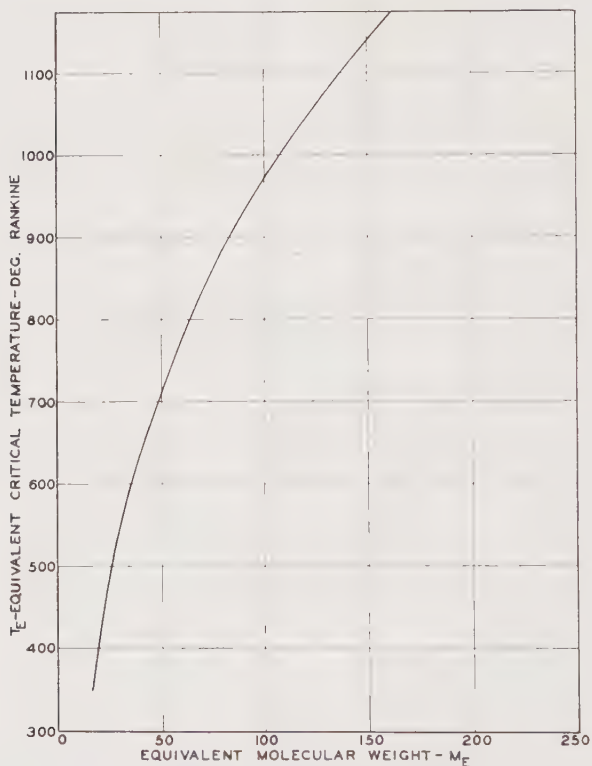


FIG. 7 EQUIVALENT CRITICAL TEMPERATURE FOR HYDROCARBON MIXTURES

question may arise as to whether the true or pseudo-critical temperature of the heptane and heavier fractions should be used in this case, but it has been found that the use of the pseudo-critical temperature is both convenient and accurate in gas density calculations.²¹ If the heptane and heavier fraction has a molecular weight between 100 and 110, it is possible to use the simpler relationship of Figure 7 to obtain the pseudo-critical temperature on the equivalent critical temperature scale.

A comparison has been made between the experimental critical temperatures of this paper, the reported critical temperatures of the binary systems, and those computed by the method just described. Table VI gives these comparisons indicating an average deviation of $\pm 4.3^\circ \text{F.}$ for the volatile mixtures of this paper and $\pm 7^\circ \text{F.}$ for the binary systems presented.

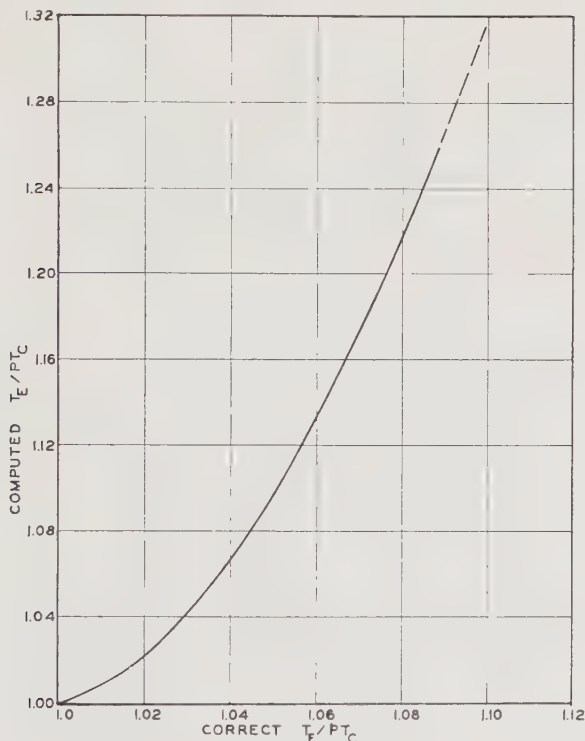


FIG. 8 CORRECTION FOR MIXTURES CONTAINING METHANE

CRITICAL PRESSURE

The first attempt for the correlation of the critical pressures was a modification of Smith and Watson's method.²⁰ This attempt did not bring the volatile mixtures into line with the petroleum fractions. It appeared that some variable which was important in the volatile mixtures, having critical pressures from 1,000 to 3,000 pounds per square inch, became rather insignificant in petroleum fractions having

relatively low critical pressures. This added variable appeared to be the molecular weight of the mixture in addition to the pseudo-critical temperature, true critical temperature, and pseudo-critical pressure

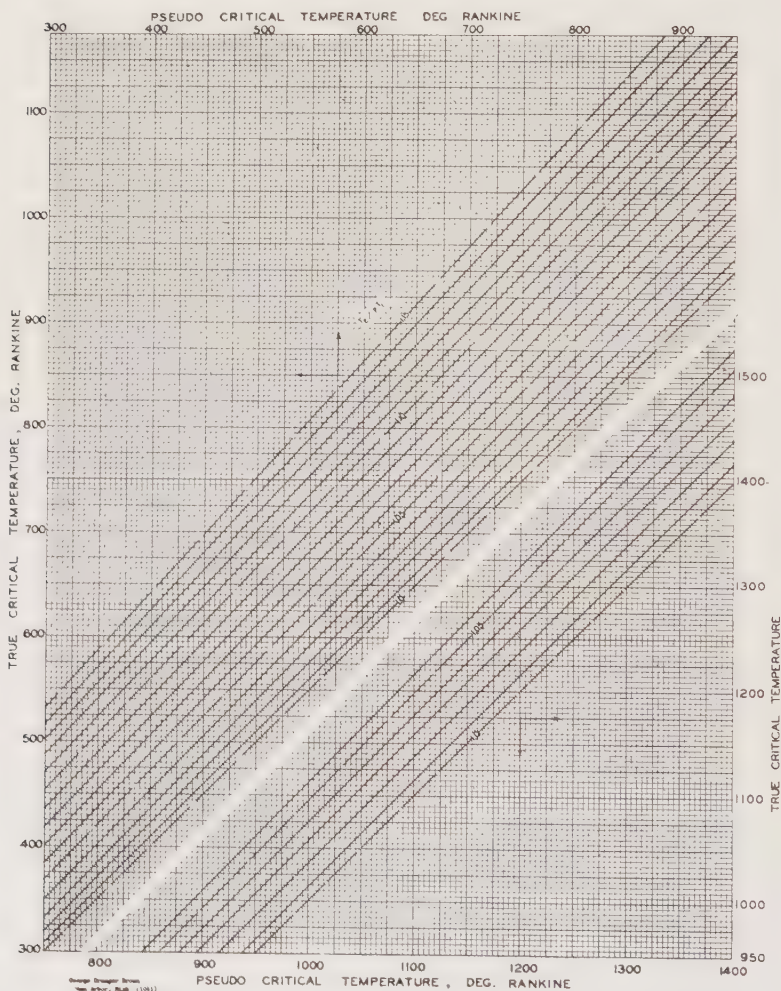


FIG. 9. Critical Temperature of Hydrocarbon Mixture.

required by Smith and Watson. The pseudo-critical pressure is computed for the mixture of known constituents by multiplying the mole fraction of the constituent by its critical pressure. Figure 10 is the

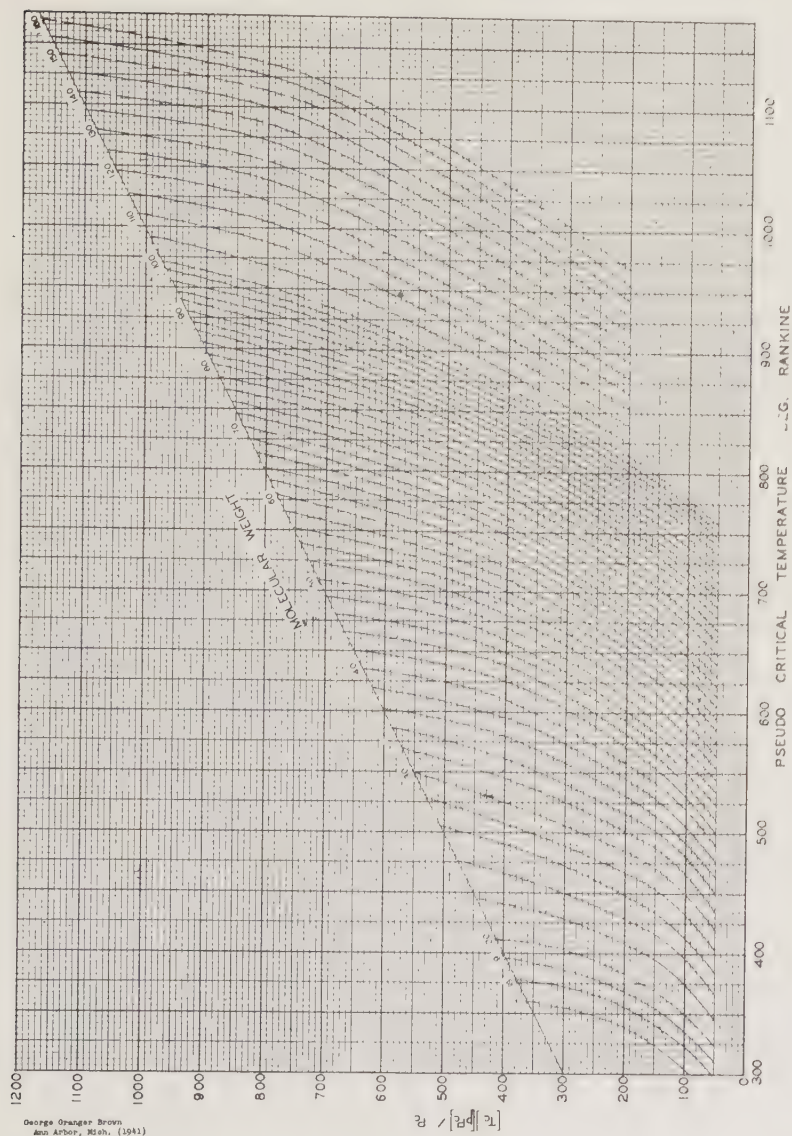


Fig. 10. Critical Pressure of Hydrocarbon Mixture.

TABLE VI.—EXPERIMENTAL AND COMPUTED CRITICAL TEMPERATURES AND PRESSURES FOR VOLATILE HYDROCARBON MIXTURES

Mol. Wt.	T_c °F. Experi- mental	P_c lbs./sq.in. abs. Exp.	T_c Proposed Method	T_c Smith and Watson Method	P_c Proposed Method	P_c Smith and Watson Method
BINARY MIXTURES (Ethane- <i>n</i> -Butane Mixtures) ⁹						
53.2	283.1	646.1	275	280	645	655
45.4	237.4	780.8	224	235	786	843
39.6	191.2	841.6	182	188	820	887
35.0	147.6	827.2	142	140	798	813
31.5	108.4	759.2	109	105	740	767
ETHANE- <i>n</i> -HEPTANE MIXTURES ⁸						
81.4	468.2	682	466	477	690	875
58.9	373.9	1106	376	376	1105	1431
46.0	276.8	1263	273	285	1230	1580
37.9	189.8	1132	191	192	1065	1232
32.2	120.3	850	120	123	807	927
PROPANE- <i>n</i> -BUTANE MIXTURES ¹⁴						
55.1	290.4	588	286	285	580	564
53.3	280.2	609	273	278	583	613
50.8	264.4	630	255	263	597	649
48.2	243.5	638	237	227	607	negative val.
46.0	224.4	631	221	220	609	608
PROPANE- <i>n</i> -PENTANE MIXTURES ¹⁸						
62.2	339.0	608	344	341	610	649
56.4	300.9	648	303	305	635	681
49.8	255.8	671	245	258	658	692
49.0	250.4	664	240	249	641	670
<i>n</i> -PENTANE- <i>n</i> -HEPTANE MIXTURES ²						
84.4	450	422.5	450	456	431	461
79.1	427	477.5	425	429	473	513
92.9	488	475.0	484	490	487	518
METHANE-PROPANE MIXTURES ¹⁶						
41.2	196.0	765	195	159	783	neg. value
38.4	178.3	890	179	160	947	798
35.6	159.7	1020	158	164	1060	1180
32.8	138.8	1160	140	128	1180	1176
30.0	115.4	1293	116	106	1270	1363
27.2	88.0	1408	89	87	1385	1607
24.4	50.7	1469	54	50	1420	1640
METHANE- <i>n</i> -BUTANE MIXTURES ¹⁷						
45.9	266.0	1093	240	250	1060	1125
38.0	217.7	1537	185	208	1443	1709
32.4	163.9	1799	139	179	1720	2360
28.3	110.1	1901	103	111	1890	2110
25.1	59.2	1924	66	74	1770	2200

Ave. Dev. 7.0° F. 30.0 lbs.

TABLE VI.—Continued

COMPLEX MIXTURES							
Mixture	Mol. Wt.	T_c °F. Exp.	P_c lbs./sq.in. abs.	T_c °F. Pro- posed Method	T_c °F. Smith and Watson Method	P_c lbs./ sq.in. abs. Pro- posed Method	P_c lbs./ sq.in. abs. Smith and Watson Method
S-2	25.0	55.0	2387	60	89	2160	3120
S-3	29.5	109.0	2574	112	140	2585	2475
S-4	29.1	109.0	2537	109	142	2540	2940
S-5	36.1	169.5	2615	167	205	2680	2700
T-1	24.5	54.0	2605	57	80	2640	3020
T-3	25.5	65.0	2675	68	101	2610	2910
T-4	27.6	90.0	2730	92	125	2790	3120
T-5	37.7	189.0	2900	181	225	2910	2820
B-1	27.4	78.0	1826	88	98	1840	1960
B-2	29.6	116.0	1797	113	120	1788	1955
B-3	31.2	142.0	1796	137	135	1800	1870
B-4	32.6	149.5	1706	142	146	1705	1775

Ave. Dev. 4.3° F. 42 lbs.

relationship devised to give the critical pressure from these four variables. Table V completes the example calculation of the critical pressure for mixture S — 3, giving 2,585 pounds per square inch abs. as compared to the experimental value of 2,574 pounds.

A comparison between the experimental and computed critical pressures for the binary systems and the complex mixtures accompanies the comparison of critical temperatures in Table VI. The average deviation for the binary mixtures is 30 pounds per square inch and for the volatile mixtures is 42 pounds per square inch which is considerably better than the method of Smith and Watson for these volatile mixtures.

For mixtures containing petroleum fractions it is necessary to use the method of Smith and Watson to obtain the pseudo-critical pressure of such petroleum fractions and insert this pseudo-critical pressure in Table V. Figure 11 is a reproduction of Smith and Watson's chart for predicting pseudo-critical pressures of petroleum fractions from either the characterization factor and cubic average boiling point or the molecular weight and mean average boiling point of the fraction.

For nonparaffinic mixtures, a method was devised for computing the critical properties by including the characterization factor^{23,24} as

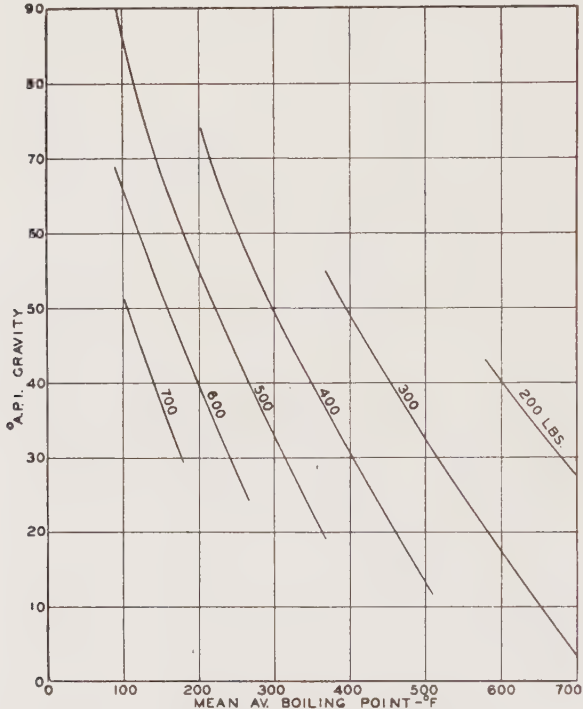


FIG. II PSEUDO CRITICAL PRESSURES OF PETROLEUM FRACTIONS

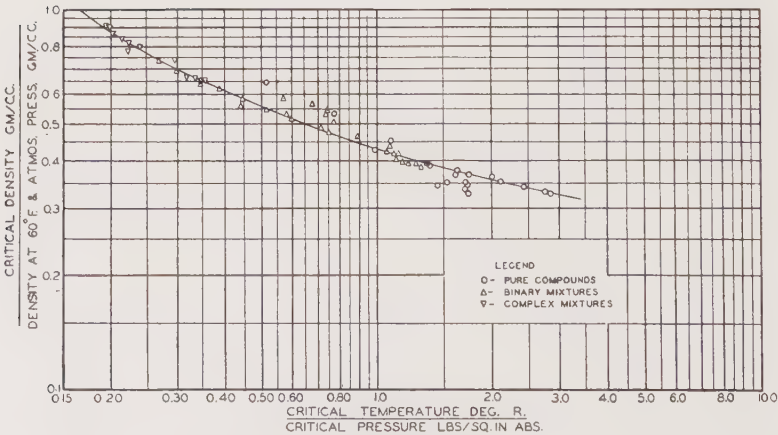


FIG 12 CRITICAL DENSITIES OF HYDROCARBONS

a variable. This adaptation reproduced Roess' data¹⁵ and the properties of pure compounds as satisfactorily as Smith and Watson's correlation for critical temperatures but was less satisfactory for critical pressures.

CRITICAL DENSITIES

No correlation for the critical density of mixtures of hydrocarbons was found in the literature. Early works on the critical densities of pure compounds^{3,19} were not applicable to volatile hydrocarbon mixtures. Also, Mathias' Law of Rectilinear Diameters is not applicable to complex mixtures because the densities of the saturated liquid and vapor do not form symmetrical curves approaching the critical density.⁸

The critical density has been found to be a function of critical temperature, critical pressure, and the apparent density of the material at 60° F. and 1 atmosphere. An apparent density of 0.25 g./cc. for methane and 0.40 g./cc. for ethane was used. Figure 12 is a plot of the ratio of the critical density to the density at 60° and 1 atmosphere vs. the ratio of the critical temperature to the critical pressure. The general function seems to apply for pure hydrocarbons and for mixtures. Methane, ethane, and propane are the pure compounds above the curve while the aromatic and cyclic compounds lie below the curve. Table VII gives a comparison of experimental and computed critical densities using Figure 12.

TABLE VII.—EXPERIMENTAL AND COMPUTED CRITICAL DENSITIES
COMPLEX VOLATILE HYDROCARBON MIXTURES

Mixture	$\rho_{cg/cc}$ Experimental	$\rho_{cg/cc}$ Computed Fig. 12	$\rho_{cg/cc}$ Computed from Compressibility Factors
S-2	0.289	0.289	0.288
S-3	0.317	0.327	0.312
S-4	0.304	0.322	0.304
S-5	0.281	0.358	0.344
T-1	0.319	0.315	0.289
T-3	0.319	0.314	0.297
T-4	0.325	0.329	0.298
T-5	0.366	0.366	0.357
B-1	0.273	0.264	0.255
B-2	0.265	0.267	0.253
B-3	0.271	0.274	0.239
B-4	0.277	0.273	0.255

A second method of computing the critical density of the mixture is the use of the compressibility factor of gaseous substances. Since the pseudo-critical temperature of a mixture is normally less than the true critical temperature, it is possible to have the true critical temperature at some value above pseudo-reduced temperature of one. This permits the use of the compressibility factor plot normally in use for computing the density of gaseous substances to obtain the density of the mixture at its true critical temperature and pressure. This calculation of the critical density depends only upon the analysis of the mixture from which the molecular weight, the pseudo-critical temperature, and the pseudo-critical pressure, may be computed. The critical temperature and pressure at which the density is to be computed may be predicted from the above correlations. The insertion of the compressibility factor into the ideal gas equation completes the calculation of the critical density by the second method. Table VII gives a comparison of the critical densities of the mixtures of this investigation when computed by the compressibility factor method using the compressibility factors for natural gases.²¹

NOMENCLATURE AND UNITS

- T_c = True critical temperature, ° R.
 T_E = Equivalent critical temperature, ° R.
 pT_c = Pseudo-critical temperature, ° R.
 P_c = True critical pressure, lbs./sq.in.abs.
 pP_c = Pseudo-critical pressure, lbs./sq.in.abs.
 ρ = Density, g./cc.
 ρ_c = Critical density, g./cc.
 M_E = Equivalent molecular weight

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